

X-RAY STUDIES OF METAL – SUPPORT INTERACTIONS IN CATALYSTS

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INTRODUCTION

The support plays a number of roles in supported metal heterogeneous catalysts. Besides assuring mechanical integrity of the system it must have an open pore structure providing access to the active phase and may also be an active component through its surface acid properties. The support may also directly affect the properties of the metal phase through what is usually classed as 'metal – support interaction'.

In the case of cobalt catalysts for the Fischer–Tropsch reaction, with metal particles several tens of nanometers in diameter, many supports have been compared. Varying conclusions have been drawn as to the effect of the support on the activity and selectivity of these catalysts. Although in a study by Bartholomew [1] the catalytic activity of supported cobalt varied in the order $\text{Co/TiO}_2 > \text{Co/SiO}_2 > \text{Co/Al}_2\text{O}_3$, Bessel [2] obtained a higher activity for alumina support than for silica while Iglesia et al. [3] found no effect on changing the support. Different activation and operating conditions were however used for these studies. Little information is available on how the support and the activation procedure influences the structure of the cobalt which forms the active phase of this type of catalyst.

The activity of alumina supported palladium catalysts, used for selective hydrogenation reactions, has been shown to reach an optimum for particle sizes of about two nanometers [4]. Although particle sizes below two nanometers would allow an increase in available surface palladium, a decrease in catalytic activity is observed. This has been attributed [5] to the loss of metallic character of the palladium atoms due to an increased effect of the metal–support interaction for small particles. Recent studies in our laboratory show that using palladium nitrite rather than the conventional palladium acetylacetonate as precursor can lead, for palladium particles of the same size, to increased catalytic activity for sub-nanometer particles. It is therefore of interest to determine the possible differences in metal–support interaction induced by changes in the precursor.

One of the major obstacles in obtaining this type of information resides in the fact that the catalysts must be studied in their reduced state. In this study the effect of the metal–support interaction on the structure of the metallic phase has been studied using two in-situ X-ray techniques : X-ray diffraction (XRD) and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. The former is well adapted to the case of Fischer–Tropsch catalysts with a large particle size. For the small particles and metal loadings below 1% typical of hydrogenation catalysts no lines due to the metal are observed by XRD. EXAFS is particularly useful in this case as the technique is element specific and no long range order is required.

MATERIALS AND METHODS

Fischer–Tropsch catalysts were prepared by incipient wetness impregnation of TiO_2 , SiO_2 and Al_2O_3 using aqueous solutions of cobalt nitrate. The samples were dried in air and calcined at 573 K before characterisation. XRD showed that the only crystalline form of cobalt present was Co_3O_4 and the corresponding particle sizes were determined by line broadening. Details of cobalt loading, specific surface area and Co_3O_4 particle size are given in table 1.

Catalyst	Co loading (% wt.)	Specific surface area (m^2/g)	Co_3O_4 particle size (nm)
Co/TiO_2	11.3	16	75
Co/SiO_2	13.0	460	14
$\text{Co/Al}_2\text{O}_3$	10.5	180	20

Table 1 : Characteristics of the cobalt catalysts

Supported palladium catalysts with a metal loading of 0.3 % wt. were prepared by incipient wetness impregnation of alumina ($130 \text{ m}^2/\text{g}$) using palladium bis-acetylacetonate in toluene (this solid is referred to as $\text{Pd}[\text{acac}]$) or a mixture of palladium nitrate and sodium nitrite with a 1:4

molar ratio of Pd/NO₂ (referred to as Pd[NO₂]). After drying the solids were calcined at 623K. Transmission electron microscopy studies showed no evidence for particle sizes greater than 1 nm in both cases.

XRD studies of Co/SiO₂ and Co/Al₂O₃ were carried out using Cu (K α) radiation on a Siemens D501 $\Theta - 2\Theta$ powder diffractometer equipped with an Anton Parr reaction chamber adapted to allow Fischer-Tropsch reactions to be carried out [6]. Reduction studies were carried out under hydrogen flow, ramping the temperature up to the desired value at 5K/min then keeping the temperature stable during XRD analysis (4 hrs). CO conversion data was obtained in-situ at 473K using synthesis gas (H₂/CO = 9, 3 bar, 8.5 g.h.l⁻¹). The silica support is amorphous allowing the XRD pattern due to cobalt phases to be clearly identified. For the poorly crystallised alumina sample an XRD pattern of the support without cobalt was subtracted after normalisation. In the case of Co/TiO₂ the presence of many sharp lines from the support (rutile and anatase forms) prevents the cobalt phases from being correctly analysed. This sample was studied using the anomalous diffraction effect at the Laboratoire pour l'Utilisation de Rayonnement Electromagnétique (LURE, Orsay) on the H10 beam line using synchrotron radiation from the DCI storage ring running at 1.85 GeV with an average current of 250 mA. The difference pattern of XRD data recorded at energies far from (7614 eV) and close to (7715 eV) the cobalt K edge allowed the cobalt phases to be isolated.

EXAFS data for the Pd catalysts were obtained on the EXAFS4 beam line at LURE, in transmission mode through a double crystal Si(111) monochromator using two ion chambers as detectors. The EXAFS reactor cell, identical to that designed by Lytle et al. [7], allows *in situ* treatment of samples at temperatures up to 773 K. The sample was reduced under flowing hydrogen using a temperature program (5K/min). The Pd K-edge region was analysed using a standard data analysis package [8]. For analysis of local environment, the EXAFS was first transformed from k space to r space (k³, Hamming windows 2.8, 4.3, 11.3, 12.7 Å⁻¹) to obtain the radial distribution function (RDF). The EXAFS spectrum for the first co-ordination shells was isolated by inverse Fourier transform of the RDF over the appropriate region and fitted using the single scattering EXAFS equation. Amplitude and phase functions for fitting Pd-O and Pd-Pd shells were obtained respectively from Pd(acac) and Pd metal foil references.

Pd catalysts were tested for buta-1,3-diene hydrogenation in a laboratory batch reactor at 10 bar, 290K with gas chromatography analysis of products.

RESULTS

a) cobalt catalysts

Reduction of the Co₃O₄ phase under hydrogen proceeds via the formation of CoO to the formation of metallic cobalt [6]. The XRD pattern after reduction at 773K shows the presence of both fcc and hcp forms of cobalt. Comparing the XRD patterns of the Co/SiO₂ and Co/Al₂O₃ catalysts at a 673K (figure 1) shows that the degree of reduction differs for the different supports.

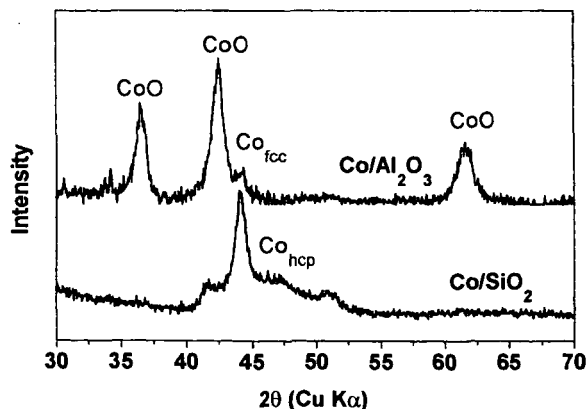


Figure 1 : In-situ XRD patterns of Co/SiO₂ and Co/Al₂O₃ at 673K under hydrogen

The silica supported catalyst is more strongly reduced at 673K than the $\text{Co}/\text{Al}_2\text{O}_3$ sample. This is in agreement with temperature programmed reduction studies showing that Co/SiO_2 is fully reduced at this temperature whereas $\text{Co}/\text{Al}_2\text{O}_3$ shows (as does Co/TiO_2) hydrogen consumption up to much higher temperatures.

The support also has an influence on the relative intensities of the diffraction peaks corresponding to the two forms of metallic cobalt (figure 2). The samples in which the cobalt is reduced only at higher temperatures show an increased proportion of fcc structure compared to hcp cobalt.

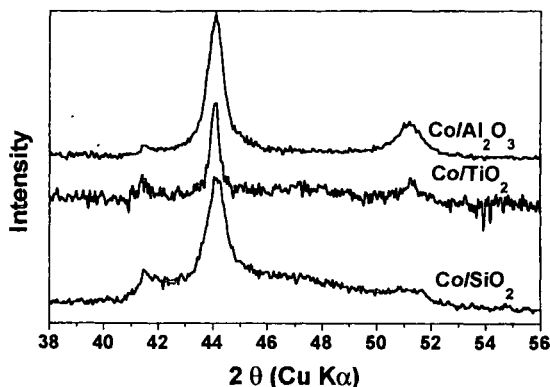


Figure 2 : XRD patterns of the cobalt catalysts reduced at 873 K

Carrying out the Fischer-Tropsch reaction in the XRD cell showed a CO conversion at 50 hrs time on stream of 25% for Co/SiO_2 whereas those of $\text{Co}/\text{Al}_2\text{O}_3$ and Co/TiO_2 were 15% and 14% respectively. On the working hypothesis that the reduction temperature was related to the cobalt microstructure developed, protocols were developed to modify the reduction temperature for a given support. By heating the calcined samples in nitrogen it was possible to stabilise the CoO form on silica at high temperature (823 K). Introducing hydrogen at this temperature provoked the reduction of CoO to metallic cobalt. It was indeed found that reduction at high temperature led to the preferential formation of fcc form. A lowering of the reduction temperature was achieved by adding ruthenium to Co/SiO_2 (impregnation of the calcined sample with ruthenium nitrate in aqueous solution to a loading of 0.3% wt). This sample was found to be fully reduced at 673 K with a majority of hcp cobalt. Figure 3 compares the structures obtained for Co/SiO_2 using these two protocols with that obtained by reduction under hydrogen. Modifying the temperature at which the metallic cobalt is formed clearly leads to controlled variation of the microstructure.

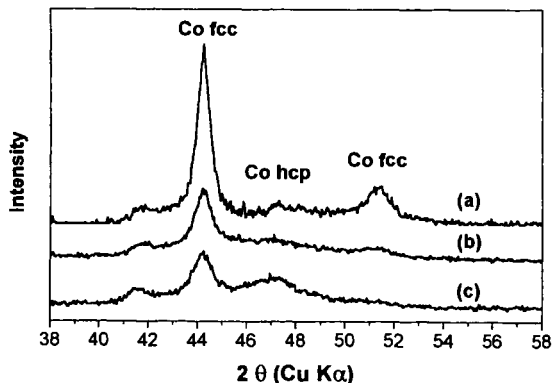


Figure 3 : Comparison of cobalt forms for Co/SiO_2 for (a) high, (b) medium and (c) low temperature reduction protocols.

Activities for the conversion of CO in the Fischer-Tropsch reaction of Co/SiO₂ samples containing different fcc/hcp ratios were significantly different. Promoted Co/SiO₂ (with a high hcp component) showed a two-fold gain in activity compared with Co/SiO₂ whereas the high temperature fcc form showed a two-fold reduction in CO conversion.

b) palladium catalysts

After reduction the sample Pd[NO₂] shows an EXAFS spectrum very similar to Pd metal foil, but of reduced intensity (figure 4). Modelling of the filtered data (inverse Fourier transform window : 1.5 to 3.0 Å) allows the average number of first nearest neighbours to be estimated as 5 +/-1, consistent with the existence of particles less than one nanometer in diameter.

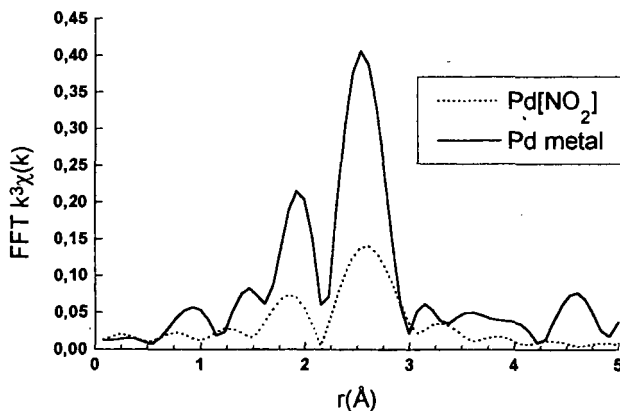


Figure 4 : RDF of the Pd[NO₂] catalyst compared to that of a Pd metal foil

The RDF of the Pd[Acac] sample is compared with that of Pd[NO₂] in figure 5. The Fourier transformed data clearly shows, in addition to Pd-Pd neighbours, a peak at low distances for Pd[Acac]. Modelling of the filtered data (inverse Fourier transform window : 0.95 to 3.0 Å) reveals this peak to be due to oxygen atoms, the average Pd-O co-ordination number being three at a distance of 1.95 Å. Pd-Pd co-ordination is similar so that particle size can be considered practically unchanged.

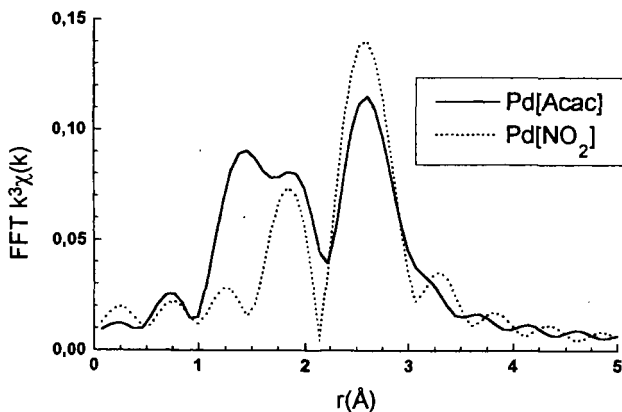


Figure 5 : Comparison of RDFs of the Pd[NO₂] and Pd[Acac] catalysts.

Buta-1,3-diene hydrogenation tests showed that the activity of the Pd[NO₂] catalysts for conversion to butene, 14 mole/min/g(Pd), was over ten times that of the Pd[Acac] catalysts, 1.2 mole/min/g(Pd), with an activity per surface Pd atom close to that obtained by Boitiaux et al. [4] for large palladium particles.

DISCUSSION

In the case of cobalt based Fischer-Tropsch catalysts the support clearly influences both the reducibility of the precursor oxide and the structure of the metal phase obtained after reduction. Our study shows that these effects are linked, and that it is the temperature of reduction that determines the fraction of different cobalt structures in the active catalyst. Modification of the reduction temperature by stabilising the intermediate oxide to high temperatures or by adding a promoter to induce reduction at low temperature enables the microstructure to be controlled. Thus, although it is not yet clear how the various oxide supports influence the temperature of reduction, the parameters controlling the activity of the final catalyst should probably be considered in the light of an oxide-support rather than a metal-support interaction. The catalytic results show that differing ratios of the two cobalt phases, fcc and hcp, lead to differing activities in the conversion of CO. Further work is required to investigate whether the differences can be attributed to intrinsic activities of the two phases or if, as suggested by Srinivisan et al. [9], it is the presence of defects induced by the presence of stacking faults in the cobalt particles that generates the active sites.

The X-ray absorption results for the Pd[NO₂] sample show the palladium in reduced samples to be in an environment close to that of bulk metallic palladium. Although the Pd-Pd co-ordination number is reduced due to the small particle size, no evidence of a well defined particle-support interaction is observed. It is clear on the contrary that the palladium in the Pd[acac] sample is in strong interaction with the support. Comparison of the catalytic results of the two systems clearly demonstrates that for conventional methods of preparation it is the metal-support interaction which leads to a reduction of activity in the case of small particles. The small Pd[NO₂] particles show similar activity to large particles for which the metal-support interaction would be diluted.

CONCLUSIONS

In-situ XRD and EXAFS have allowed the microstructure of catalysts in the active state to be characterised and give an insight into the parameters controlling the activity of the metallic phase. In the case of large cobalt particles, XRD shows differences in microstructure as a function of the support that can be rationalised in terms of reduction temperature. This has allowed protocols to be defined that lead to controlled microstructures whose presence can be directly correlated to activity in Fischer-Tropsch synthesis. EXAFS studies of small palladium particles demonstrate that the activity of hydrogenation catalysts can be clearly linked to the presence or absence of metal-support interaction. Control of this interaction can lead to higher activities for small particles and thus to more efficient catalysts.

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